University of Delaware
Newark, De 19716-3820
Ph: 302/831-6200
Fax: 302/831-6226
www.udel.edu/iec

INSTITUTE OF ENERGY CONVERSION

UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

October 4, 2006

Bolko von Roedern
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12
D.5.6

Dear Bolko:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period from July 16, 2006 to August 15, 2006, under the subject subcontract. The report highlights progress and results obtained under Task 1 (CdTe-based solar cells).

Task 1 – CdTe-based Solar Cells

Summary

During this reporting period, effort continued on high throughput fabrication of thin film CdTe/CdS cells with CdTe deposited by vapor transport (VT). The CdS films were deposited by chemical surface deposition (CSD) onto 10 x 10 cm plates of Pilkington TEC15 SnO_2/glass. Particular focus was placed on Ga deposition for the high resistance (HR) Ga_2O_3 buffer layer and on the chemical state of the TCO. Analysis of the chemical state of the CdTe surface after aniline treatment continued and shows that, like other etchants, the aniline treatment removes surface-bound oxygen and chlorine, generates Te, but also may leave a trace hydrocarbon residue behind. Darshini Desai completed her doctoral research, which is summarized below, and defended her thesis.

Influence of Buffer Layer Thickness on VT CdTe/CdS Solar Cells

CdTe/CdS solar cells with CdTe deposited by VT onto TEC15 SnO_2/glass have $V_{oc} < 700$ mV and exhibit a high degree of shunting when the final CdS film thickness is less than 60 nm. We have previously shown that a thin high resistance buffer layer improves both V_{oc} and yield, for a variety of materials, such as Al_2O_3, Ga_2O_3, and i-SnO_2. For the VT baseline device, Ga_2O_3 was adopted, prepared by native oxidation of thin films of Ga, deposited by sputtering from a liquid Ga target, which proved difficult to control. We reported (July 2006) on success using Ga films deposited by electrodeposition from aqueous solution. The Ga films are easily prepared in a highly controllable and repeatable manner. The solution consists of 1 mM $GaCl_3$ in 0.1M KCl.

To determine the deposition potential, we evaluated the cyclic voltametric (CV) response of the bath and substrate using 2" x 1" samples of TEC15. Pt gauze was used as the auxiliary electrode, and a saturated calomel (SCE) reference electrode was employed. The voltage scan rate was 50 mV/s, and the solutions were Ar-purged prior to use. No stirring, bubbling or agitation was used during measurement. Figure 1 shows the CV response of the aqueous KCL solution (blue) and of the same with the $GaCl_3$ added, with the cathodic current represented as positive.

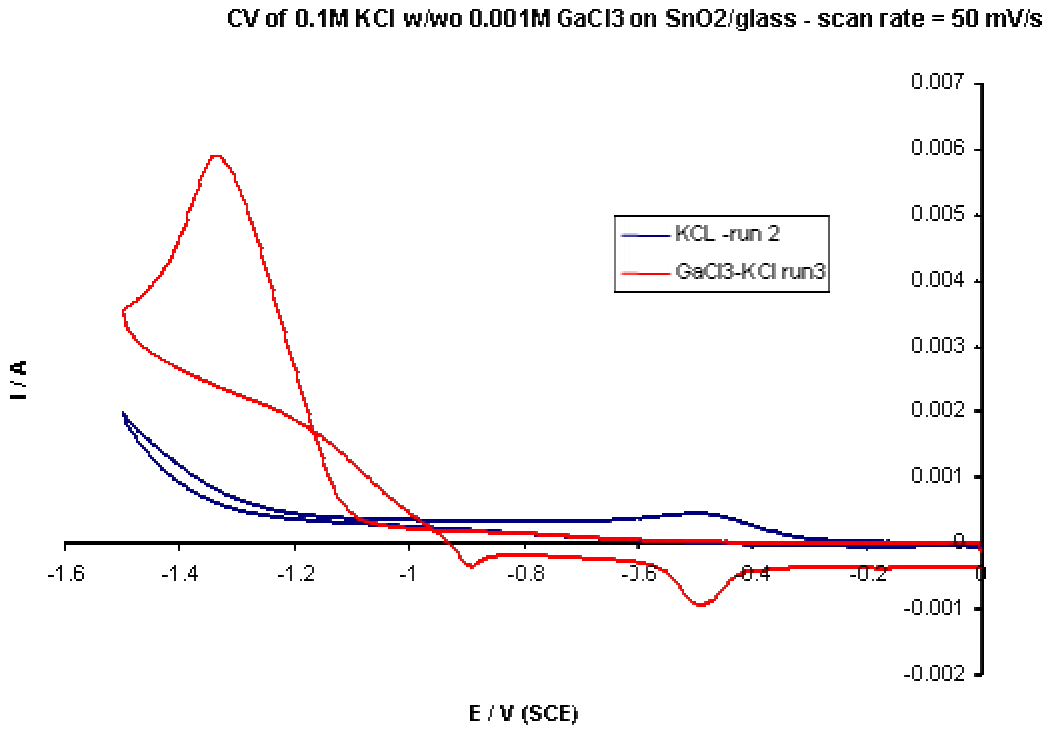


Figure 1. Cyclic voltammogram of 0.1M KCl solution (blue) and of the same with 0.001M $GaCl_3$ (red) on TEC15 SnO_2/glass. The scan rate was 50 mV/s and temperature was 25°C.

In the figure, the solution with only KCl exhibits the expected behavior, with cathodic current onset at V < -1.2 V (SCE) corresponding to the decomposition of water. The solution with $GaCl_3$ exhibits cathodic current onset at V < 1.1 V due to Ga reduction: $Ga^{+3} + 3e^- \rightarrow Ga^o$. From this, a deposition potential of -1.2 V was selected, to give reasonable deposition current while remaining outside the decomposition range for water. For baseline VT cell fabrication, the 10 cm x 10 cm substrates are coated in freshly prepared 2 L baths containing 1mM $GaCl_3$ + 0.1M KCl at room temperature. Uniform Ga deposition was obtained without stirring, and consideration of the chemical reaction and the average current density showed a mean Ga deposition rate of 3 nm/min. The deposition time was varied in 5-minute increments for evaluation of the optimum Ga thickness in devices. Table I lists the best-cell performance and yield for 1" x 2" samples cut from each 10 cm x 10 cm plate having identically deposited CdTe and identical post-deposition processing: 2 minute vapor $CdCl_2$ treatment; aniline etch; and Cu/Ni contacts. Note that oxidation of the Ga to Ga_2O_3 reduces the film density by 2%, so that the Ga thickness is approximately the same as the Ga_2O_3 film thickness (the densities of Ga and Ga_2O_3 are 6.095 g/cm^3 and 5.94 g/cm^3, respectively).

Table I. JV performance for recent VT CdS/CdTe devices on TEC15 having different preparation and HR layer properties. All samples had standard CdS. Yield is defined by the number of cells with low shunt conductance, i.e. $G_{sc} < 5$ mS/cm^2.

Sample	Glass/ SnO_2	Ga thickness (nm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff. (%)	Yield
VT242.1	TEC15	0	650	25.8	74.6	12.5	3/8
VT237.1	TEC15	15	737	23.8	70.0	12.3	7/8
VT238.1	TEC15	30	776	23.9	68.7	12.8	8/8
VT239.1	TEC15	45	691	24.5	53.7	9.1	8/8
VT240.1	TEC15	60	726	24.6	65.3	11.7	6/8
VT244.1	TEC15	30	766	24.5	65.0	12.2	8/8
VT243.1	TEC15	30**	730	24.1	75.4	13.3	7/9

** TEC15 was put through the soap/rinse step twice prior to the Ga deposition.

In the table, the upper group shows V_{oc} and yield maxima for cells with 30 nm Ga, which is in the same range found for sputtered Ga and evaporated Ga. In spite of this, the best V_{oc} in the group is less than 800 mV. The FF, on the other hand, is maximum for no Ga and for 15 nm thick Ga and is counter to results obtained earlier and to results for PVD cells. We suspected and verified by XPS that contaminants were being introduced to the TCO surface during the soap/rinse steps prior to Ga deposition. The lower group in the table shows the effect of doubling the exposure of the TCO to the soap/rinse process prior to the Ga deposition, resulting in likewise degradation of the V_{oc} and enhancement of the FF. A systematic iterative investigation is underway to identify and control deleterious chemical species.

Back contact is facilitated by a short etch in aqueous aniline solution, which has been discussed in detail in previous reports. Depth profile XPS analysis of the surface of VT CdTe films after $CdCl_2$ treatment and then after aniline treatment was carried out to determine the composition from the exposed surface to a depth of ~30 nm. Cd/Te and O/(Cd+Te) ratios were shown in the previous report. The XPS measurement conditions were described in the previous report. Elemental compositions are shown here in Table II.

Table II. XPS compositional analysis of VT CdTe in as-deposited condition, after 2 minute $CdCl_2$ treatment at 480°C and after subsequent *ex-situ* etch in aniline for 4 minutes.

Condition	Depth (nm)	Cd (%)	? Te (%)	? O (%)	Cl (%)	C (%)
As deposited	0	25	20	34	0	21
$CdCl_2$ treated	0	33	26	10	10	21
Aniline etched	0	22	35	8	0	35
As deposited	13	48	45	7	0	0
$CdCl_2$ treated	13	48	50	0	2	0
Aniline etched	13	46	52	0	0	1

The upper group in the table, for the exposed film surface, suggests elevated Te and C concentration after aniline etching compared to the as-deposited and vapor $CdCl_2$-treated cases. The Te coverage is not uniform however, based on the strong Cd signal obtained. The lower

group, after Ar^+ milling for 10 minutes, shows Cl penetration after vapor $CdCl_2$ treatment, and slight Te and C enrichment after aniline etching. These observations are consistent with the photoactivated aniline-CdTe reactions that remove lattice Cd, leave elemental Te, and form a hydrocarbon polymer. The reaction rate is often not uniform in polycrystalline CdTe films, leading to lateral variations in Te thickness. The key observation, which accounts for this, is that the Te production rate is highest for $CdCl_2$-treated films and at locations on the films, which received the highest $CdCl_2$ dose during the treatment. The higher observed Te production rate is likely due not to higher Cl levels but rather due to higher electrical conductivity, facilitating greater charge transfer during the etch process.

CdTe/CdS Device Operation

Darshini Desai has been working on bifacial device analysis and effect of stress conditions on CdTe solar cells during the past 5 years as part of her graduate program in electrical engineering. She defended her dissertation on August 17, 2006. The abstract from her dissertation summarizes her work and is listed below.

Thin film CdTe based solar cells have the potential for high efficiency and have been investigated for 30 years due to their variations in flexibility in manufacturing technology, rapid deposition, and an excellent match to the solar spectrum. Despite these promising attributes, these devices have not reached their full potential. Their large scale implementation is limited by several factors, including back contact and stability issues. The device performance is not well co-related with different design parameters and to date, there is no generally accepted model for carrier transport.

Fabricating ohmic contacts to a p-type CdTe cells, due to its high work function, has been a long-standing problem in the photovoltaic industry. Many different contact materials and processes have been developed, but still, the contacts at their best are quasi-ohmic. In this work, a semi-transparent back contact using Cu doped ZnTe film was developed by galvanic deposition. This novel bifacial device configuration with transparent ZnTe:Cu back contacts permitted us to perform bifacial device characterization by illuminating the device through either the front or back contact or simultaneously through both. This approach to device characterization, using a bifacial device, is novel contribution in the field of thin film CdTe photovoltaic characterization techniques because it allows us to accurately determine the fundamental minority carrier transport parameters such as the diffusion length (L) and depletion width (W), and separate effect of front junction from the back contact. The cells used for this project were produced by different methods but had similar efficiencies ~10-12%, even though the processing conditions and back contact fabrication techniques and materials varied.

Bifacial current voltage (JV) analysis of illuminated devices indicated that the back contact was photosensitive. Experimental results prove that CdTe device operation is controlled solely by the primary CdS/CdTe heterojunction. Detailed bifacial spectral analysis on devices made with different CdTe thicknesses, and different applied biases was used to quantify the transport parameters L and W. CdTe devices with absorber thickness in the range of 3-8μm were investigated. The diffusion lengths derived were in the range of 0.6-0.7μm. In CdTe devices, the absorption co-efficient is in the range of 10^5 1/cm, W in the range of 2-4μm. As a result the absorption depth $\alpha W > 1$, and all the carrier generation and absorption occur in the depletion

region even for forward bias of 0.5V. Bifacial spectral response characterization results prove that for CdTe solar cells, the operation is determined by voltage dependent current collection and not diffusion length.

Laboratory simulated accelerated test life conditions were used to investigate the cell degradation phenomenon, with direction towards identifying device degradation mechanisms. Stressing results show that primary degradation in efficiency occurs due to degradation in the open circuit voltage (V_{oc}) and the fill factor (FF). Cyclic stress, where in the devices were subjected to alternating light and dark light bias cycles and switching applied bias during stress experiments performed on CdTe devices, allowed us to identify and partially explain transient degradation and recovery mechanism in CdTe devices. Results from stressing experiments performed on CdTe devices made with different back contact materials showed that cells with ZnTe:Cu based contacts had minimum degradation in V_{oc}. Bifacial JV analysis performed on these stressed devices revealed a photo-sensitive back contact.

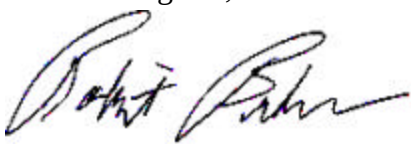
Temperature dependence of the open circuit voltage with different back contacts was studied under different illumination conditions. Measurements showed there were two distinct regions, one above 220K where open circuit voltage linearly increases with temperature, and one below 200K where V_{oc} becomes nearly independent of both temperature and light intensity. A model explaining this "V_{oc} saturation " behavior has been proposed in this document.

Photovoltaic device modeling results obtained using AMPS (analysis of microelectronic and photonic structures) suggest that the dominant recombination mechanism is the SRH recombination through midgap states.

Collaboration and Publications

A single VT deposition was carried out on four NREL CdS/HR/TCO samples to compare differences in CdS deposition conditions. Device results will be discussed in the next report. A paper on the design of VT deposition is published: "Design of a vapor transport deposition process for thin film materials," G. M. Hanket, B. E. McCandless, W. A. Buchanan, S. Fields, and R. W. Birkmire, J. Vac. Sci. Technol. **A 24**(5) Sept/Oct 2006 1695-1701.

Best regards,



Robert W. Birkmire
Director

CC: Kevin Dobson, IEC
Steve Hegedus, IEC
Brian McCandless, IEC
Paula Newton, IEC w/report
Susan Tompkins, OVPR, UD
Carolyn Lopez, NREL w/report